

FIRST QUARTERLY PROGRESS REPORT  
CdS PHOTOVOLTAIC FILM CELLS

HARSHAW CHEMICAL COMPANY

31 August 1962

OTS PRICE

XEROX

\$

2.60 ph.

MICROFILM

\$

0.83 mf

*T. A. Griffin and F. A. Shirland*

FIRST QUARTERLY PROGRESS REPORT

*Title*

RESEARCH AND DEVELOPMENT  
IN  
CdS PHOTOVOLTAIC FILM CELLS

by

T.A. Griffin and F.A. Shirland

CA.

THE HARSHAW CHEMICAL COMPANY  
CLEVELAND, OHIO

3920006

Period of 1 June 1962 to 31 August 1962

31 August 1962

*4 refs*

(NASA Contract No. NAS 3-2493)

*OTS: HJ.60ph, \$0.83mg*

*(NASA CR-51210)*

CHEMISTRY AND ENERGY CONVERSION DIVISION  
LEWIS RESEARCH CENTER  
NATIONAL AERONAUTICS AND SPACE ADMINISTRATION  
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*LB*

# FOREWORD

The work of this project has been carried out at the Solid State Research Laboratory of the Harshaw Chemical Company, at 2240 Prospect Avenue, Cleveland, Ohio. Project direction has been provided by Mr. F. A. Shirland. Mr. T. A. Griffin has acted as the Project Supervising Engineer and Principal Investigator.

The following personnel have contributed to the work of this Contract and charged time approximately as indicated during the period June thru August, 1962.

Name	Duties	Hours
F. A. Shirland	Project Direction	97½
T. A. Griffin	Project Supervision	297
J. C. Schaefer	Chemical Engineer- Arrays Fabrication	97½
R. W. Olmsted	Physicist-Design and Testing	367
F. Feko	Technician-Film Evaporation	174
B. Szymanski	Technician-Array Fabrication	147
M. Williams	Technician-Cell Fabrication	203½
T. Orseno	Technician-Film Evaporation	157½
A. Tanos	Technician-Cell Fabrication	142½
	TOTAL	1683½

It is estimated that the project is 47% complete as of August 31, 1962.

# TABLE OF CONTENTS

	<u>Page</u>
INTRODUCTION AND SUMMARY . . . . .	1
PILOT LINE . . . . .	1
EVAPORATION EQUIPMENT . . . . .	2
SUBSTRATES . . . . .	2
EVAPORATED FILMS . . . . .	3
COLLECTOR ELECTRODE . . . . .	4
OHMIC CONTACTS . . . . .	14
WORK PLANNED FOR NEXT PERIOD . . . . .	15
REFERENCES . . . . .	17

## LIST OF FIGURES

<u>Figure</u>		<u>Page</u>
1	Silver Collector Grid . . . . .	6
2	I-V Characteristic Curves For Cell X-14 With Different Collector Grids . . . . .	7
3	Electrical Test Circuit For Measurement of Barrier Sheet Resistance . . . . .	8

## LIST OF TABLES

<u>Table</u>		<u>Page</u>
I	Effect of Substrate Temperature on Front Wall CdS Film Cell Output . . . . .	5
II	Comparison of Collector Grid Spacings . . . . .	10
III	Barrier Sheet Resistance Measured With Cells in Various Ambients after Various Treatments . . . . .	11
IV	Evaluation of Various Metals for Collector Grids . . . . .	12
V	Effect of Ag and Cu Collector Grids Held In Pressure Contact to Cells Without Application of Heat . . . . .	13

## INTRODUCTION AND SUMMARY

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This report covers the first three months of work on a six month research and development contract on CdS thin film photovoltaic cells sponsored by the Lewis Laboratory of NASA with Dr. Andrew E. Potter acting as contract monitor. This work is part of a continuing project, much of which has been sponsored by the U.S. Air Force under several contracts, and reported separately. (1,2,3)

In this work, efforts have been concentrated in several specific areas requiring more detailed study than had been possible previously. These areas include: the collector contact to the barrier region of the CdS evaporated front wall film cell; the ohmicity of the contact between the evaporated CdS film and various metallic foil substrates; and the optimization of vacuum evaporation conditions used to deposit the CdS film. Appreciable progress in each of these areas is reported.

### PILOT LINE

During the first half of this contract a standard process line for making CdS front wall solar cells was operated. This line provided a base line to evaluate advances. It also provided an opportunity to gain an understanding of and a tighter control of the parameters involved in the process. The expense of operating this line was shared by the USAF and NASA, since both are supporting research involving work on the CdS front wall film cell. There were about 150 evaporated film cells fabricated on this pilot line during the first three months. After the cells were fabricated and tested they were used for other tests e.g. life tests, lamination experiments, etc. Periodically, glass rear wall cells were also fabricated on this line to furnish a continuous measure of front wall cell performance as compared to the rear wall operation. The 150 odd front wall film cells fabricated on the pilot line in this period averaged 0.9% in conversion efficiency when tested in equivalent terrestrial sunlight. This was somewhat lower than had been obtained previously and the reason for this is believed at least partially attributable to the higher humidity prevalent in the summer months. There has been a definite correlation between relative humidity in the laboratory and average cell efficiency.

These cells were all contacted with a grid pattern of conductive silver paint applied by hand with a ruling pen. This method of contacting is known to yield cells with appreciable internal series resistance, and much of this resistance has been suspected to be the sheet resistance of the barrier layer which the silver paint stripes do not minimize. A major portion of the effort of this contract was planned for the study of this series resistance and indicated steps to reduce it. This study was successful and has resulted in an alternate method of contacting the cells which appears to yield cell efficiencies more than double that obtained by the older method. This work is described later in this report.

## EVAPORATION EQUIPMENT

At the initiation of this contract, a new Kinney vacuum evaporator was ordered. This equipment has arrived, and has been installed and tooled for operation. This evaporator will increase the number and variety of evaporations and other experiments that can be performed.

A new type of filament has been installed, that is calculated to reduce pin holes and splattering. This is a tantalum filament sold by Allen-Jones Company of Long Beach, California. It was developed for the evaporation of  $\text{SiO}_2$ , and is designed so that the vaporized material enters a chimney through small holes in the side of the chimney. Thus particles would have to first get through the small holes, then make a  $90^\circ$  turn before they could strike the substrate and cause pin holes in the film. This effectively prevents the impingement of these small unvaporized particles on the substrate.

Some work is planned for evaluation of the substrate heater. Presently, the substrates are heated by radiation from a molybdenum strip resistance heater. Since the substrate is also molybdenum it is feasible that it can also be used to supply its own heat by passing current through it. Resistance heating may provide a more uniform heating of the substrate, and be more readily and accurately controlled.

## SUBSTRATES

When the CdS polycrystalline film cell was first reduced to practice it was found that fairly thick films, on the order of 50 to 100 microns, were required. It was believed that evaporated films of such thickness would have to be laid down on substrates that closely matched CdS in thermal expansion properties, or the films would flake off the substrate when cooled to room temperature after evaporation. For this reason, the first film cells were made on pyrex glass substrates, and the first front wall film cells were made on molybdenum substrates - both materials matching CdS fairly closely in thermal expansion coefficient.

However, as part of an earlier NASA supported program, it was found that other metals could successfully be used as substrates for CdS vacuum evaporated films - at least under some conditions. It appeared that the major factor was that the metal of the substrates, if it did not match CdS in thermal expansion coefficient, must be soft or ductile so that it could not exert excessive stresses on the CdS film when a temperature change occurred. Part of the scheduled effort of this contract is to investigate various metal foils as CdS film cell alternate substrate materials. Silver and zinc have been studied in this period and compared with molybdenum.

Silver foil .0005" thick was not usable by the present techniques. CdS films approximately .002" thick were made on .0005" silver and the CdS cracked off of the substrate. However, .001" thick silver was satisfactory. Cells were made on .001" Ag foil that were 1.7 and 1.8% efficient. The reasons for this apparent anomaly are not clear, though it is possible that some tempering of the thinner material may have been present, or that

some work hardening occurred in processing the .0005" thick foil. Good cells were also made on .001" thick zinc substrates.

For the majority of cells made on molybdenum in this period .002" molybdenum was used. However, .001" thick molybdenum can be used, although it requires more careful handling, and does give some occasional trouble with curling. Generally in this case, better results are obtained when the CdS film thickness is also reduced.

These three substrate materials were selected to be used first. Films that have been produced on them are being used for measurements of the ohmicity between the CdS and the Mo, Ag & Zn. Other metals such as Au, Cu, Al, Cd, Sn, will also be used, after it is determined how to make the best contact to the CdS. It may prove necessary to use a thin inter-layer of In or Cd between the CdS film and the substrate in order to effect a good ohmic contact to some of these metals.

Some work has been done and more will be done comparing the different surface preparations of these substrates. For instance, chemical etch and sandblasting have been used on all three of the above mentioned metals. An even chemical etch seems superior since it gives a clean surface. However, sandblasting seems to produce cells with less tendency to curl. Sandblasting may aid by pre-stressing some of the thinner substrates, but it also deforms the thinner soft metals very greatly - particularly the .0005" silver substrates.

#### EVAPORATED FILMS

One method of increasing the power-to-weight ratio of thin film photo-voltaic cells is to decrease the weight of the cells. Most of the weight of the CdS thin film cell array is in the substrate. However, it has been found that molybdenum foil substrates, and other metal foil substrates, when made thinner give trouble with excessive curling of the CdS film-substrate combination. It has appeared that in order to minimize difficulty with curling, the CdS film and metal substrate must be of approximately the same thickness.

Thus, the key to higher watts per pound by lighter weight construction seems to be the successful use of thinner CdS films. At first, very thick CdS films, in the range of .003 to .005" were needed because thinner films gave excessive shorting between the barrier region and the substrate, with consequent low shunt resistance of the cells. As improved vacuum evaporation procedures, and improved methods of cleaning the substrates were developed, the CdS film thickness was successfully reduced to just under .002". Occasionally, film thicknesses of .001" have given good cells, but this has been an exception rather than the rule. Part of this study therefore is directed towards determining the factors which would permit the use of thinner CdS evaporated films

One method of making thinner evaporated films is to raise the substrate temperature while using the same source charge and temperature. There is



a possibility that this would produce a better structured film since the deposition rate would be reduced while the time remained the same. The higher substrate temperature would give more of an annealing affect with possibly larger grain growth. A series of films were made by varying the substrate temperature in steps between 100°C and 280°C. The thickness of the films ranged from .001" to .002". Little difference in the cells made from these films was apparent. They were all on .002" molybdenum. The cells and their properties are listed on Table I. Ordinarily, CdS films as thin as .0015" or less have displayed poor shunt characteristics when fabricated into cells. Therefore, it looks as if thinner films can be used if they are made at elevated substrate temperatures. If both the substrate and the CdS thickness can be reduced while maintaining cell efficiency, the watts per pound can be greatly increased.

#### COLLECTOR ELECTRODE

During the period just prior to the beginning of this Contract it was found that a much improved collector contact could be made to CdS front wall film cells by laminating a fine mesh-shaped metallic grid in place of the hand-ruled conductive silver paint grid. These mesh-shaped grids were obtained from the Buchbee-Mears Company, of St. Paul, Minnesota. They are made from thin metallic foils by etching away most of the metal leaving only a fine network pattern such as is illustrated in Figure 1. They are available in a variety of metals and spacings of the grid lines.

The result of this improved contact was a lowering of series resistance and an improvement in the shape of the I-V characteristic curve, as is shown in Figure 2. Thus, cell efficiencies were more than doubled in most cases.

While the initial work on this collector electrode was done on a separate Air Force Contract, continuation of this work was carried out on the present contract and attempts were made to determine experimentally the effect of different mesh geometries and different grid materials.

In order to determine the optimum mesh size, an attempt was made to measure the sheet resistance of the barrier. The problem was to eliminate the effect of the conducting layer of molybdenum and n-type CdS in the measurements. The electrical test circuit used for this measurement is shown in Figure 3. The average sheet resistance as measured on a number of barriers was about 1000 ohms per square. Since the mathematical solution of the equivalent circuit of a distributed series resistance cell involves a non-linear differential equation, an attack of the problem was made by an empirical method. The average value of sheet resistance was determined. Knowing this, an optimum electrode spacing could be calculated for any size collector electrode. At this optimum the decrease in series resistance obtained by moving the collector stripes closer together and adding a stripe would be balanced by a loss in output due to the decrease in active area covered by the extra stripe. It was determined that for a sheet resistance of 1000 ohms per square, 20 lines per inch should give the optimum grid spacing.

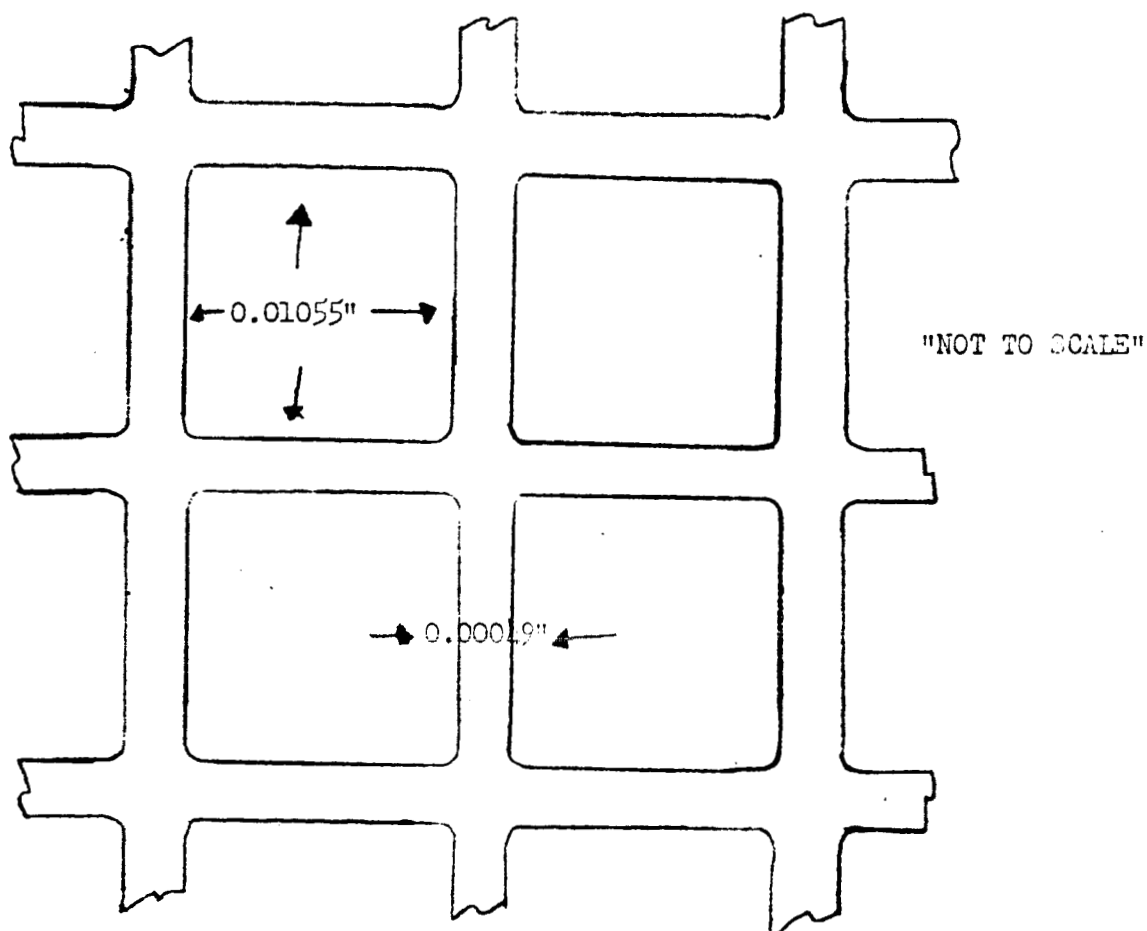
At the time this contract was initiated, two Ag meshes were on hand.

TABLE I

EFFECT OF SUBSTRATE TEMPERATURE ON FRONT WALL  
CdS FILM CELL OUTPUT

CELL	CdS FILM THICKNESS	SUBSTRATE TEMPERATURE	Cell Characteristics			
			OCV	SCC	AREA	EFF.
X23	.0011"	280°C	.42v	46 ma	16.1cm <sup>2</sup>	.6%
24	.0010		.46	62	16.1	.8
25	.0011		.43	55	16.1	.6
X20	.0018	220°C	.45	67	16.1	.7
21	.0019		.46	72	16.1	.8
22	.0018		.46	65	16.3	.8
X26	.0018	150°C	.45	60	16.1	.7
27	.0018		.43	57	16.1	.6
28	.0019		.44	62	16.1	.7
X29	.0018	100°C	.47	67	15.1	.8
31	.0020		.46	75	16.1	.9

FIGURE 1  
SILVER COLLECTOR GRID

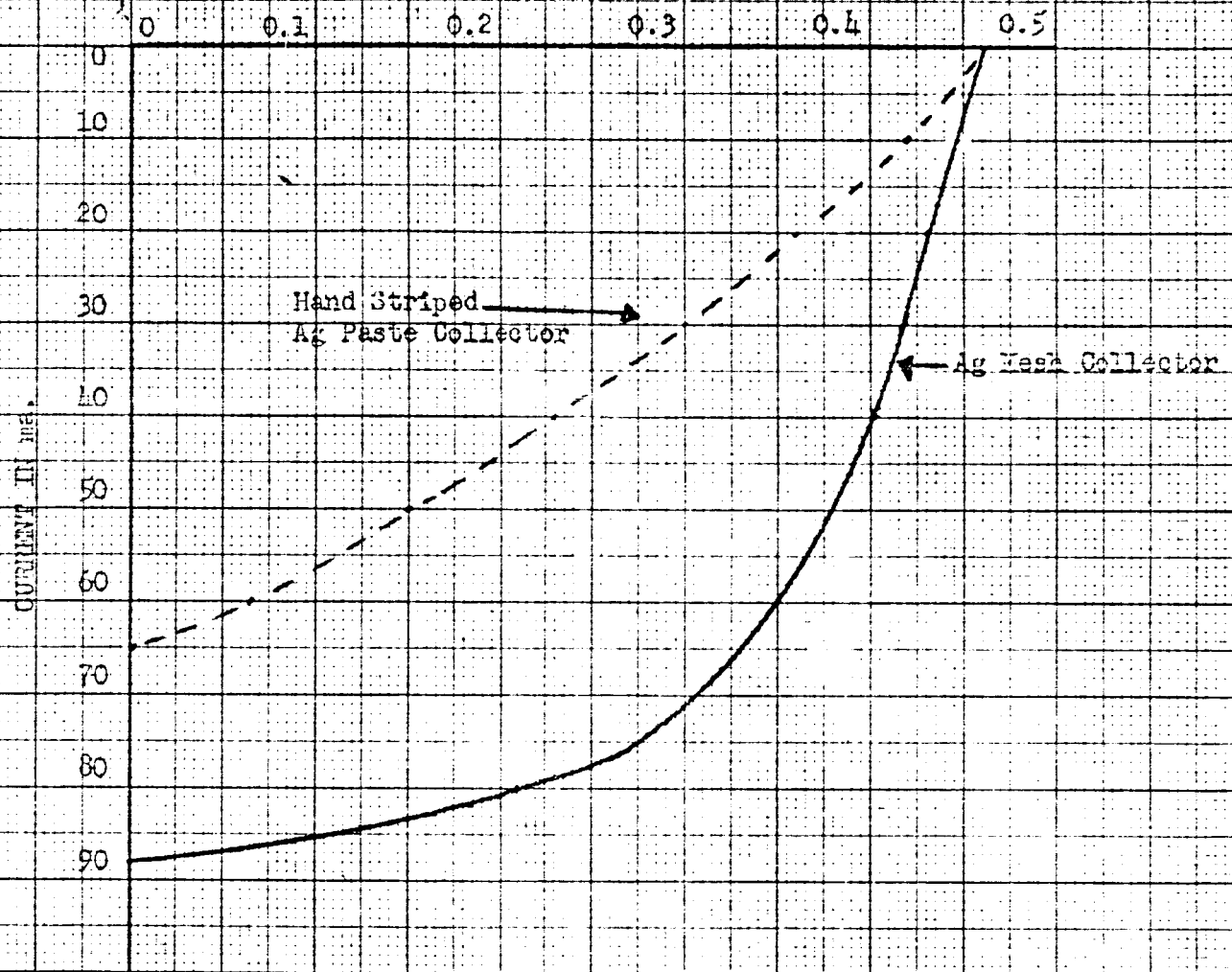


Ag Mesh 0.0005" thick  
90 lines per inch  
90% transmission

FIGURE 2

I-V CHARACTERISTIC CURVES FOR CELL X-11  
WITH DIFFERENT COLLECTOR GRIDS

Illumination =  $100 \text{ mw/cm}^2$

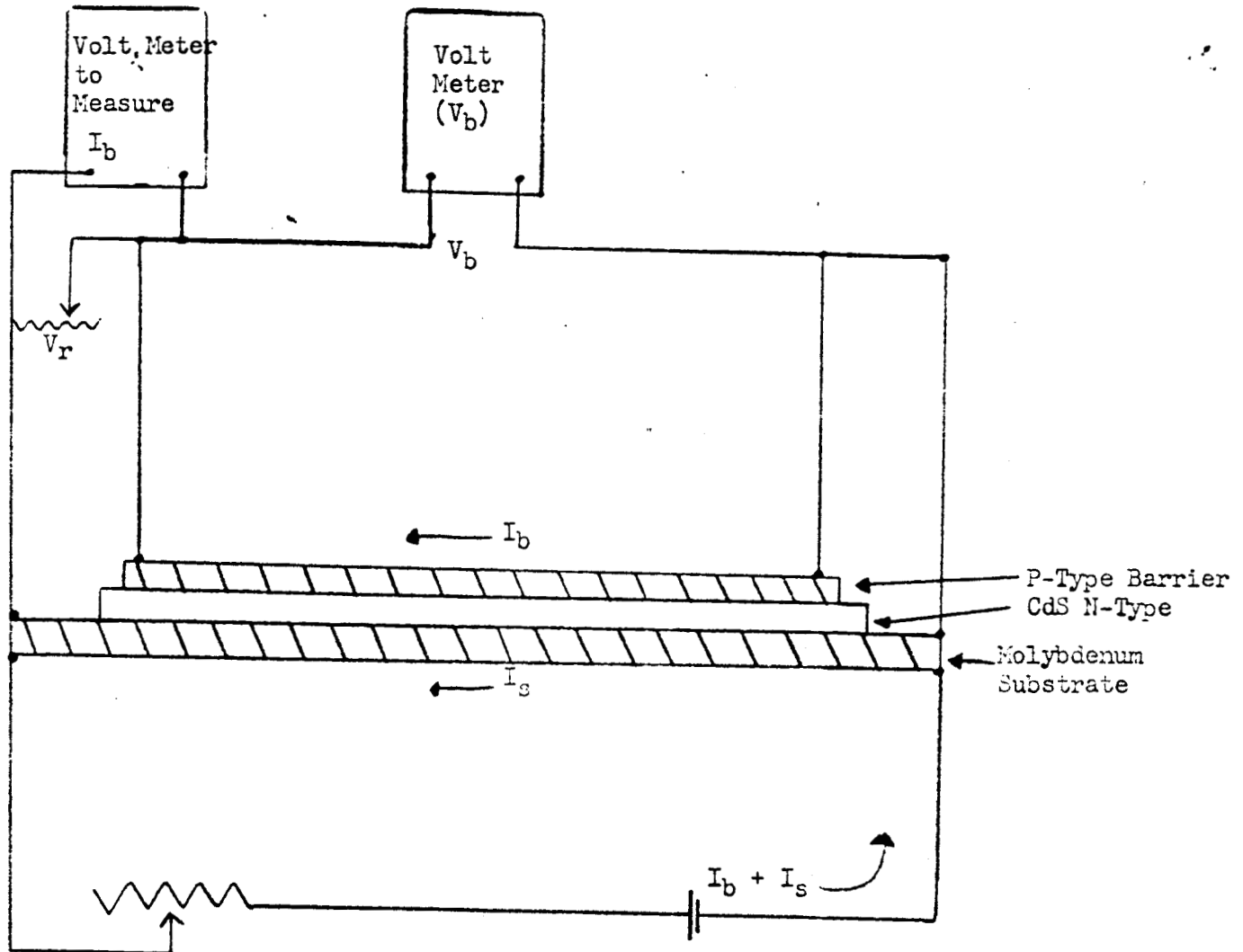


Cell X-11, CdS on Molybdenum Substrate

Collector	OCV	SCC	Area	Efficiency
Ag Paste	0.46 V	65 ma	$11.9 \text{ cm}^2$	0.8%
Ag Mesh	0.46 V	68 ma	$11.9 \text{ cm}^2$	1.86%

FIGURE 3

ELECTRICAL TEST CIRCUIT FOR MEASUREMENT OF BARRIER SHEET RESISTANCE



$I_b$  = Current through barrier layer

$I_s$  = Current through molybdenum substrate

$V_b$  = Voltage across barrier layer

$V_r$  = Voltage across current measuring resistor

Necessary condition  $V_b \gg V_r$

One had 70 lines per inch and a transmission of 91%. Another had 280 lines per inch and a transmission of 72%. Several cells were fabricated employing each type, and the cells were compared. The data are presented in Table II. While there is appreciable scatter of the data, the 70 lines per inch grid does appear to give a definitely higher cell efficiency.

If the calculations determining the optimum grid spacing were based on the correct sheet resistance, then the efficiency of the 280 lines per inch should have been poorer than the efficiency of the 70 line per inch group. This was found to be the case, on the average, even though one cell with the 280 line per inch grid had the highest efficiency. This higher average efficiency is reasonable considering the fact that the finer grid had 19% less transmission. Measurements of sheet resistance were made on several films. The circuit was the same as that described in Figure 3, previously. It was found that more than the initial sheet resistance of the barrier was involved. There appeared to be changes in the barrier sheet resistance due to subsequent treatment. Therefore, the steps in the process were separated. The measurements were made in air, in vacuum, over desiccant, in vacuum with heat, under pressure as experienced in lamination, and with plastic laminated to the surface. Table III shows the results of this series of measurements. There was a large increase in sheet resistance when plastic was allowed to flow under pressure against the barrier region. There was only slight increases in sheet resistance under the other conditions. Exactly what was occurring is not yet clear, since the above data were not sufficient to pin down the factors involved. Perhaps the plastic is isolating small islands of the barrier region. More data must be collected in order to establish what is happening and how it affects cell contacting.

There is a possibility that the various sizes of silver mesh do not laminate the same under identical conditions, and also that different metals might act differently under the conditions of lamination. While silver is the best conductor, other metal meshes including copper, gold and nickel were available, so they were also tried. Some of these are much more economical than the silver and some may make better ohmic contact to the barrier. Table IV lists some of these tests.

The indicated conclusion from these data is that Cu and Ni are not satisfactory materials for collectors, and that Au is as good, or better, than Ag. Previous experience with CdS single crystal cells indicates that all of these metals should make a good contact to the CdS barrier. Thus, this test does not make much sense unless some other factor came in to play with the Cu and Ni meshes. One such possible factor might arise from the nylon interlayer between the mesh and the Kel-F. If the screen got too warm during the lamination, there is a possibility that it might float away from the surface up into the nylon and give a rather high contact resistance. The I-V curves of the cells with Cu collector looked as if they had a poor contact at the collector, that is, they displayed high series resistance.

In order to eliminate such a possibility of flowing plastic a test set up was made to duplicate the lamination conditions, but without the heat. A chamber was provided with a window. The metal mesh was placed below the window, then the cell below that. A diaphragm under the cell had air pressure applied to it. This pushed the cell against the mesh. Two leads, (one to the mesh and one to the molybdenum) were used to lead the power out when light was allowed to enter through the window. Table V shows the result of Cu and Ag meshes tested in this manner. The Cu mesh collector was much

TABLE II  
COMPARISON OF COLLECTOR GRID SPACINGS

CELL	TYPE OF Ag FOIL COLLECTOR	COV	SCI	AREA	EFF.
83FN	70 lines per inch	.43V	97 ma	11.4cm <sup>2</sup>	1.8%
89FN		.43	136	15.8	2.21
87FN		.44	98	15.6	1.52
94FN		.45	90	15.9	1.58
92FN		.47	92	15.8	1.57
				AVERAGE	1.75%
82FN	280 lines per inch	.46	100	12.4	2.36
88FN		.43	92	15.8	1.35
86FN		.46	88	15.6	1.29
91FN		.46	78	15.9	1.16
93FN		.46	80	19.7	1.28
				AVERAGE	1.48%

TABLE III

BARRIER SHEET RESISTANCE MEASURED WITH CELLS IN VARIOUS  
AMBIENTS AND AFTER VARIOUS TREATMENTS

CELL	IN AIR	IN VACUUM	HEATED		UNDER PRESSURE	LAMINATED WITH NYLON	LAMINATED WITH KELL-F
			IN DESICCATED AIR	IN VACUUM			
588	2.13	(3.3)-3.2	(3.7)-3.7	(2.0)-3.3			
642	0.73	(0.7)-0.87	(0.48)-0.53	(0.51)-0.36			2.26
644	0.33	(0.33)-0.33					
589	0.97					4.3	
627	2.10					3.5	
659	0.76					2.0	
668	0.39	(0.37)-0.37	(0.38)-0.38	(0.35)-0.29			2.1
669	0.73				(0.65)-0.65		(0.43)-.68
676	0.53	(0.65)-0.65			(0.57)-0.62		(0.4)-.865
679	0.60				(0.53)-0.67		(0.41)-1.62
S-7	0.93					66.5	
S-16	0.60					2.26	
S-17	0.42					2.32	

NOTES:

Values in parantheses are those taken just before film was subjected to a change e.g. just before it was put into vacuum, or heated etc., while those not in parentheses were taken after the change.

All resistance measurements were taken in the dark.

All values in thousands of ohms per square.



TABLE IV  
EVALUATION OF VARIOUS METALS FOR COLLECTOR GRIDS

CELL	TYPE OF COLLECTOR	OCV	SCI	AREA	EFFICIENCY
84FN	70 lines per inch Cu	0.15V	2 ma	12.3cm <sup>2</sup>	0.00
85FN	" " "	0.47	22	15.6	0.18%
95FN	" " "	0.3	11	15	0.00
90FN	70 lines per inch Ni	0.3	2.2	15	0.00
96FN	" " "	VERY HIGH SERIES RESISTANCE			0.00
136FN	70 lines per inch Au	0.51	116	15.3	2.2%
137FN	" " "	0.5	112	15	2.1%
138FN	" " "	0.47	124	15	2.2%
89FN	70 lines per inch Ag	0.43	136	15.8	2.2%

TABLE V

EFFECT OF Ag AND Cu COLLECTOR GRIDS HELD IN  
PRESSURE CONTACT TO CELLS WITHOUT APPLICATION OF HEAT

Cell Characteristics

CELL	MESH	OCV	SCI	AREA	EFFICIENCY
X60	70 lines per inch Ag	0.48V	100 ma	15.9 cm <sup>2</sup>	1.45%
X60	70 lines per inch Cu	0.48	93	15.9	1.2
X58	70 lines per inch Ag	0.5	51	15.9	.75
X58	70 lines per inch Cu	0.5	48	15.9	.48

better than when laminated. The lower efficiency when compared with silver was due to a higher series resistance. This may be inherent in the Cu, since silver is a better conductor, or just due to the fact that the Cu is not as soft as the silver and therefore did not conform to the barrier surface as well as the Ag.

Because of the success of this test, a piece of test equipment will be built that will more closely duplicate the lamination. This will enable films to be tested without the necessity of being laminated or hand striped. They can then be stored, and matched as they are needed for arrays. This test set up is presently being designed and will be fabricated. Using this test equipment, much time can be saved since a permanent collector will not have to be put on each cell before it is tested. It should supply a ready means to compare the various metals and mesh sizes. This will also yield a goal to strive for in the lamination of each mesh. This is very important since it now seems that each mesh laminates differently.

#### OHMIC CONTACTS

The last phase worked on this first period was the ohmicity of the contact of CdS with various metals that might be used as substrates. Only a beginning was made on this testing. The results so far are preliminary.

In attempting to detect nonlinearities in the contact between the molybdenum substrates and the evaporated cadmium sulfide film, indium-mercury contacts were used. Indium makes a good contact to N-type CdS according to several investigators<sup>(4)</sup>, and corroborated in this laboratory.

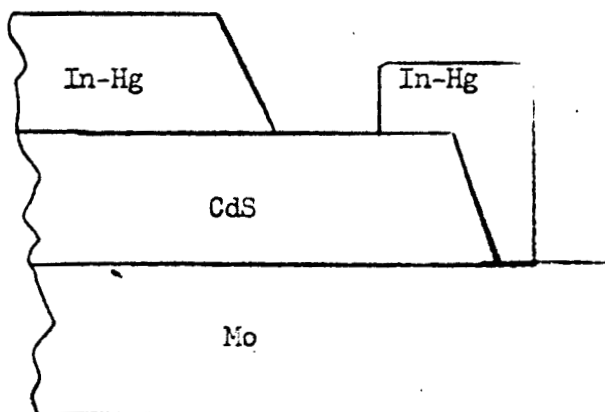
On one sample, a very low-voltage nonlinearity was noticed. It may have been due to tunneling between the In-Hg and the CdS, or it may have been caused by the test equipment. At a higher voltage, 0.1 volts p-to-p, the I-V trace appeared fairly linear. At 0.2 volts peak to peak, a curvature was noticed in the forward part of the I-V trace. At 0.8 volts p-to-p, some curvature appeared in the "reverse" direction. These nonlinearities could have been associated with the Mo-CdS contact. Because the CdS film evaporated onto molybdenum may have unique properties, it cannot be certain that the In-Hg makes an ohmic contact to the film.

There are a number of possible ways to determine whether or not the resistance of the In-Hg-CdS contact is linear. One way would be to remove a portion of the CdS film from the molybdenum and apply two In-Hg contacts. This will be attempted using a method employed in electron microscopy using "victawet" or B<sub>2</sub>O<sub>3</sub> between the CdS and molybdenum, and nitrocellulose against the surface to free the film from the molybdenum without cracking it.

Another possible way to get an indication of the behavior of the In-Hg contact on evaporated CdS films is to compare tests on cells with different substrates. Preliminary tests showed that the I-V curves of cells on molybdenum begin to curve first in the forward direction, as indicated above (that is, when the In-Hg electrode is positive). On silver substrates, the bend appears at the other end of the I-V curve (when the In-Hg electrode is negative). On a zinc substrate, the I-V curve seems to be linear.

It was suggested that if two In-Hg electrodes were applied to the CdS film, one at the edge and one very close to it, then the conductivity of the molybdenum substrate might not effect the evaluation of In-Hg electrodes.

THUS:



Another possibility is to use CdS films that have been evaporated on non-conducting glass substrates. More work will be done along these lines in the next period.

The question was raised as to what information the I-V curve gives on the contact of the CdS film with the substrate. Previously, it has been assumed that the shape of the curve stems from one non-linear junction. In order to get some experience with the behavior of more than one non-linear junction in series, various combinations of CdS film cells and single crystal cells, along with a silicon photovoltaic cell were tested. The results suggest that the change of the value of the reverse breakdown voltage in the CdS film cells might arise from the presence of two non-linear photovoltaic junctions within the cell.

#### WORK PLANNED FOR NEXT PERIOD

The pilot line will be continued, with improved methods of contacting.

The new evaporator will be placed in service. The new filament will be of a type to reduce splattering, and therefore to reduce pinholes.

Cells will be made from thinner substrates and thinner CdS films.

Attempts will be made to optimize the contact between the CdS and metal substrate, using the information gained from the ohmicity tests being made.

The optimum collector available will be selected and laminated on film barriers.

Several other metal substrates, such as Au, Cd, Sn & Ta, will be used and tested for ohmicity. The surface preparation of these substrates will be studied, e.g., mechanical cleaning vs. chemical etch.

During this period the best substrate material and the best collector will be used to fabricate the arrays required for delivery to the contract monitor.

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